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PROCEEDINGS

Evaluation of the Stress Corrosion Cracking Susceptibility of Fire Suppressant Storage Container Alloys in Replacement Candidates for Halon 1301.

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ABSTRACT

Halons 1301 and 1211 have been identified as chemicals with sufficient ozone depletion potential to warrant limitations on their production and use. Several candidates have been selected as replacements for Halon 1301 and because their behavior is not well understood, their compatibility with the alloys used in the storage and distribution systems is of great concern. The service conditions require long term exposure of these alloys to the replacement agent under high pressures and as a result, these alloys may be susceptible to environmentally assisted failures. Therefore, an evaluation was undertaken to determine the propensity for failure of any of the alloys selected for use as containment vessels by an environmentally assisted fracture mechanism as a result of exposure to the replacement candidates.

Data from *in-situ* slow strain rate tensile tests in the pure agent were used to formulate a ranking of each agent/alloy combination. The results of this ranking indicated that some alloy/agent combinations were less desirable than others, but overall, the potential for failure of the selected alloys by stress corrosion cracking (SCC) is relatively minor under the evaluated conditions. From this it was concluded that a suitable alloy can be selected for any of the replacement agents and that no agent should be eliminated from further evaluation because it promotes SCC in the containment vessel alloys. However, additional testing is required at lower temperatures, with and without the

presence of contaminates, before a final conclusion can be made regarding the susceptibility of these alloys to environmentally induced failure in the replacement candidates.

INTRODUCTION

The Montreal Protocol of 1987 identified a number of fully saturated, halogenated organic chemicals which possessed sufficient stratospheric ozone depletion potentials to warrant limitations on their production and use.(1) Two of the most common fire suppressants, Halon 1301(CF_3Br) and Halon 1211(CF_2Br_2) were included on that list. These agents have been the in-flight fire suppression agents of choice in engine nacelles and dry bay applications for many years because of their wide range of desirable properties. These include no residue after discharge, low toxicity, long term storage stability in addition to being non-corrosive and electrically non-conductive.(1)

Due the projected unavailability of these agents, there is a great need for an environmentally favorable, alternative fire suppressant.(1) The results of intensive screening evaluations by the US Air Force produced a list of twelve potential candidates to replace Halon 1301 and Halon 1211 for use as in flight fire suppressants. The twelve agents selected for evaluation were: HCFC-22, HCFC-124 HFC-227, HFC-134a, HFC-236, HFC-125, HFC-125/HFC-32 (azeotrope), FC-31-10, FC-116, FC-218, FC-318, and $NaHCO_3$. The compatibility of these replacement candidates with the variety of materials used in the storage and distribution systems is of serious concern, and as a result, an extensive analysis was undertaken to evaluate the potential for corrosion-induced failure of these materials by the candidates. The specific mode of corrosion induced failure addressed in this paper is environmentally assisted fracture. Since the service conditions require both the storage bottles and the rupture disk materials to be exposed to the replacement agent under high pressures for long times, there is great potential for failure by environmentally assisted fracture.

The environmentally assisted fracture[1] mechanism can generally be described as: the formation and propagation of a crack in a material at a stress well below that required for cracking by purely mechanical means resulting from a simultaneous exposure to a chemically reactive environment and a mechanical stress.[2,3] This form of attack occurs in

[1]In the literature, environmentally induced failure is also referred to as, stress corrosion cracking (SCC),chloride stress cracking, hydrogen embrittlement, season cracking in brass, caustic embrittlement insteels, liquid metal embrittlement (LME) and sulfide stress cracking. (2,3)

specific material/environment combinations and while its effects may not be readily apparent, failures from environmentally induced cracking can be sudden and dramatic. Therefore, a series of experiments was conducted to determine whether a replacement candidate should be eliminated from further consideration because it promotes environmentally induced fracture of the alloys, either presently in service or under consideration for future use.

EXPERIMENTAL

Experiments were designed to evaluate the propensity for a failure of one or more of the selected alloys by an environmentally assisted means in the replacement candidate agents during storage. The technique chosen for this analysis was the slow strain rate (SSR) tensile test because it generates intrinsic mechanical properties data for a given alloy and it also reveals any interactions that may have occurred between that alloy and the testing environment; all within a relatively short time frame.(4) In this technique, cylindrical specimens are loaded in tension by a slow increase in the strain until failure occurs by either normal mechanical or by an environmentally assisted means. The potential of each agent to promote environmentally induced failure is determined by comparing the load or strain necessary to cause failure in an inert environment to that required to cause failure in the agents at the same temperature.(3,4)

The materials chosen for this study were representative of the range of metals presently in service or under consideration as either as storage bottles, distribution systems or as rupture disks. These alloys included: 304 austenitic stainless steel, PH13-8 Mo stainless steel, AM-355 stainless steel, stainless steel alloy 21-6-9 (Nitronic 40), 4130 alloy steel, Inconel alloy 625, copper/beryllium alloy CDA-172, and aluminum alloy 6061-T6. The compositions of these alloys and their nominal densities are given in Table 1.

All of the samples used for this analysis were machined with the tensile axis parallel to the rolling direction of the plate stock (Figure 1) and tested in the "as received" condition.(6) The sample preparation for these experiments consisted of a measurement of the critical dimensions followed by a thorough degreasing— first in acetone and then in alcohol. The test vessels were commercially available autoclaves with a 250 ml total capacity. Modifications were made to the basic design so that a load could be applied directly to a tensile specimen *in-situ* under constantly maintained environmental conditions (5.86 ± 0.5 MPa at 150° ± 1° C). These conditions were selected because they represent the

upper extreme of the range of normal storage conditions. A schematic diagram of the test vessel is shown in Figure 2.

The appropriate mass of each agent was determined by a computer program based on the available thermodynamic data and the ideal gas law. This approach was selected for two reasons: 1) the number of moles of agent was held constant for each test; regardless of the agent used, and 2) the actual final pressure was slightly lower than the predicted value which greatly reduced the possibility of damaging a vessel. The procedure used for charging the agent consisted of first evacuating the test vessels by attaching it to a mechanical vacuum pump for a minimum of thirty minutes. Next, the test vessels were chilled in a bath of either ice and water, or dry ice and alcohol, depending on the temperature required to maintain the liquid phase of the agent. After chilling the vessels were placed on a high capacity balance to monitor the mass of the liquid agent during filling. The vessels were then slowly heated to 150 ±1 °C and held at that temperature for the duration of the test.

The mechanical tests were conducted with a computer controlled slow strain rate testing system which operated at a constant crosshead speed of 0.0254 µm/sec. The computer was configured to sample and record the applied load, the crosshead displacement, and the elapsed time at ninety second intervals[4]. After failure, the agent was released, the vessels were allowed to cool to ambient temperature, and the samples were removed from the vessel and stored in a desiccator until analyzed.

Reduction in area (RA) measurements were made on the fracture surfaces with an optical measuring microscope which had a resolution of $\pm 0.5 \times 10^{-6}$ m. The fracture surfaces were then cut from selected broken SSR samples and prepared for analysis. Scanning electron microscopy was performed on samples to verify the mode of cracking. The results of this analysis were then used to formulate a ranking of the potential for failure by stress corrosion cracking for each of the alloys in each replacement candidate.

RESULTS AND DISCUSSION

The susceptibility of a material to environmentally induced failure can be assessed by the three basic parameters generated by a slow strain rate tensile test. These are: the ultimate tensile strength (UTS), the strain to failure (STF) and the reduction in area (RA). The UTS is a measurement of the fracture strength of the alloy and it determined from the maximum load observed during the tensile test according to the

equation 1:

$$UTS = \frac{P_{max}}{A_o} \quad (1)$$

where P_{max} is the maximum load supported by the sample during the test and A_o is the initial cross-sectional area of the gauge section of the sample.(5) If cracking, or some other environmental interaction that lowers the strength, occurred, it will produce a noticeable change in this parameter. Environmental interactions can also occur with deformational processes on the surfaces and at tips of cracks formed within the sample.(3) These interactions will generally result in a reduction in the ductility. One of the two parameters used to measure the ductility is the engineering strain to failure (ε_f) which can be determined from equation 2:

$$\varepsilon_f = \frac{l_f - l_o}{l_o} \quad (2)$$

where l_f is the total change in length of the sample during the experiment and l_o is the initial gauge length.(5) This strain value includes both the elastic and plastic components necessary to induce failure. The other parameter used to measure of the ductility is the percent reduction in area. This is determined by a physical measurement of the fracture surface at the completion of the tensile test and equation 3:

$$RA = \left(\frac{A_f - A_o}{A_o} \right) 100 \quad (3)$$

where A_f is the cross sectional area of the fracture surface and A_o is the cross sectional area of the initial gauge section.(5) Unlike the engineering strain to failure, this quantity is based solely on the plastic deformation required for failure and, as a result, it is a better measurement of the environmental interactions for most engineering alloys.

The results of the UTS, STF and RA analyses are shown in Tables 2, 3 and 4 respectively. The values presented in these tables are the numerical average of three tests performed in both the replacement candidate agents and in argon at 150 °C. The values from tests conducted in laboratory air at ambient temperature are also included in these tables for comparison. The results of these measurements were then quantified by forming a ratio between the values obtained from the

test environment and those obtained from argon, the inert reference environment. (3) Statistical analyses were also performed on these data sets to evaluate the significance of the observed variations. The results of the statistical analyses were combined with the ratio values and used to generate the final agent/alloy rankings presented in Table 5.

A significant decrease in the average UTS (Table 2) may be an indication of cracking but it could also be the result of corrosion reactions which reduced the effective cross-section or the result of a flaw in the sample. In general, an increase in the average UTS data is unusual and may reflect a sample/environment interaction that inhibited deformation and/or fracture. The increases present in Table 2 could also be the result of an interference between corrosion products generated on the sample and the seal of the autoclave through which the sample must slide. The most important point reflected in the UTS data is that no agent induced significant changes in all alloys. This indicates that a suitable material can be selected for use as containment vessels and distribution systems for any of these agents.

The majority of the environment/alloy combinations shown in the STF data (Table 3) exhibited increases in the measured strain to failure as compared to the argon values. This may be an indication that deformation was easier in those agents than in pure argon at that temperature. Since environmentally induced cracking usually results in a decrease in the measured strain to failure, the results of these measurements again indicate that a suitable material can be selected for use with these agents. It is important to note that these values were based on displacements of the load frame taken by a transducer outside of the autoclave during the experiment. Therefore, the reduction in area values which are calculated from physical measurements of the final fracture surfaces are a more reliable indication in the changes in ductility.

In Table 4 it can be seen that the reduction in area is significantly reduced (greater than 10%) in four of the 96 possible alloy/agent combinations: Al-6061 in HCFC-124, Al-6061 in $NaHCO_3$, 304-SS in $NaHCO_3$, and AISI-4130 in $NaHCO_3$. Since three of these four were in the same agent, $NaHCO_3$, it can be concluded that alloys exposed to $NaHCO_3$ may have trouble with environmentally assisted fracture.

Table 5 was constructed in order to summarize the results of the slow strain rate tensile tests. This was done by assigning a numerical value to the highest (worst) score received by each agent/alloy combination. The values used for this analysis were the absolute values of the differences between the mean for the alloy in the agent and Ar

divided by the standard deviation for the alloy and test parameter at 150 °C.(3) Therefore, the ratings presented in Table 5 are measures of the significance of any postulated environmental influences on the deformation and fracture behaviors of any alloy/agent combination.(3) If the maximum deviation was less than one standard deviation, that alloy/agent combination was assigned a value of one, if it was greater than one standard deviation, but less than two, it was assigned a two, etc.(3) In this table, it can be seen that sixty-five of the 96 agent/alloy combinations received either a one or two rating. Every agent had at least one alloy with a one rating and only two agents had one alloy with a one rating. No alloy received only one's and two's in all agents and no agent received only one's and two's for all alloys. The 304 stainless steel samples demonstrated the best overall performance of the alloys by receiving a value of one in all but three of the 12 environments. HFC-236 was among the best performing agents.

These results indicate that none of the agents tested in this analysis induced stress corrosion cracking in each of the alloys examined and should not be eliminated from further consideration on that basis. Clearly, some agents were more aggressive than others and some agent/alloy combinations can be considered undesirable. However, a suitable material can be selected to contain these agents should one of them be selected to replace Halon 1301. It is important to note that this conclusion is valid only for the agent composition and temperature evaluated in this study and that the influence of contaminants (e.g., water) or residuals from synthesis should be evaluated before these materials are put into service.

SUMMARY AND CONCLUSIONS

The objectives of this analysis were: 1) to evaluate the propensity for failure of any of the alloys selected for use as containment vessels by an environmentally assisted fracture mechanism as a result of exposure to the candidate replacement agents and 2) to determine whether any of the replacement candidates should be eliminated from further consideration because they promote SCC in the containment vessel alloys. Slow strain rate tensile tests were conducted *in-situ* under extreme storage conditions in the pure agent in order to determine the susceptibility to stress corrosion cracking. The three parameters used to determine the susceptibility to SCC in this investigation (i.e., the ultimate tensile strength, the engineering strain to failure, and the reduction in area) all indicated that a suitable alloy could be identified for storage vessel and rupture disk applications for any of the twelve candidate

agents.

A statistical analysis was performed on each of the data set to determine the relative magnitude and significance of the variations observed in the data. The results of that analysis were then combined with values obtained from ratios between the environmental test results and the results obtained from tests in argon to formulate a best to worst ranking of each alloy/agent combination. The results of this ranking indicate that some alloy/agent combinations were less desirable than others, but again, a suitable alloy can be selected for any of the replacement agents.

The data used in this analysis were obtained from experiments conducted in the pure agent at relatively high temperatures. While the results of this analysis are encouraging, additional testing is required at lower temperatures with and without the presence of contaminates before a final conclusion regarding the susceptibility of these alloys to environmentally induced failure in the replacement candidates can be made.

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Table 1
Composition of the alloys in weight percent.

Element	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130
Ni	7.1	--	61.39	8.26	0.06	8.4	4.23	0.08
Cr	19.75	0.04	21.71	18.11	0.01	12.65	15.28	0.98
Mn	9.4	0.15	0.08	1.41	--	0.02	0.8	0.51
Mg	--	1	--	--	--	--	--	--
Si	0.5	0.4	0.09	0.49	0.08	0.04	0.16	0.23
Mo	--	--	8.82	0.17	--	2.18	2.6	0.16
Nb	--	--	3.41	--	--	--	--	--
N	0.29	--	--	0.03	--	0	0.12	--
C	0.02	--	0.02	0.06	--	0.03	0.12	0.32
Be	--	--	--	--	1.9	--	--	--
Co	--	--	--	0.11	0.2	--	--	--
Zn	--	0.25	--	--	--	--	--	--
Cu	--	0.15	--	--	97.9	--	--	--
Fe	bal	0.7	3.97	bal	0.06	bal	bal	bal
Al	--	bal	0.23	--	0.04	1.11	--	0.04
g/cm^3*	7.83	2.70	8.44	7.94	8.23	7.76	7.91	7.85

* Nominal Density

Table 2
Average Ultimate Tensile Strength (MPa) in Each Agent at 150 °C as Compared to Ar at 150°C and Air at 25°C.

Environment	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130
Lab Air	627	341	957	773	763	1117	1005	6[illegible]3
Hot Ar	610	240	927	667	874	1136	969	647
HCFC-22	606	228	901	674	821	1161	932	612
HCFC-124	624	235	937	648	860	1027	945	665
FC-31-10	617	235	910	649	841	1176	935	673
HFC-227	610	235	911	667	865	1156	928	650
HFC-125	611	235	924	650	847	1154	917	669
FC-116	601	230	939	695	817	1128	942	653
HFC-134a	618	225	932	653	851	1144	929	683
HFC-236	612	245	930	633	861	1168	935	648
FC-C318	595	289	924	519	851	1182	950	445
FC-218	624	235	944	681	842	1170	928	663
HFC-32/125	639	227	913	693	844	1138	916	641
NaHCO3	623	252	947	643	852	1217	953	674
Alloy Avg.	615	239	926	650	846	1152	934	640
Std. Dev.	16	16	22	37	22	44	15	350

Table 3
Average Strain to Failure (%) in Each Agent at 150 °C as Compared to Ar at 150°C and Air at 25°C.

Environment	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130
Lab Air 49.9	13.0	44.4	30.3	13.0	5.9	10.7	8.3	
Hot Ar	41.5	7.9	41.0	13.6	10.1	6.2	9.2	7.9
HCFC-22	30.3	6.6	31.6	12.5	12.0	7.6	9.5	8.1
HCFC-124	36.0	10.5	43.7	14.1	12.4	7.9	9.1	8.2
FC-31-10	34.3	10.1	37.2	12.4	12.9	6.5	7.8	8.0
HFC-227	37.8	10.7	42.6	13.6	11.7	6.9	9.6	7.7
HFC-125	40.4	9.8	43.4	15.1	11.6	6.7	9.8	8.1
FC-116	40.6	9.1	44.3	10.2	12.9	6.1	8.6	8.5
HFC-134a	37.7	9.4	46.5	12.7	10.1	7.7	9.2	7.8
HFC-236	36.3	9.7	41.5	16.9	9.7	7.0	9.7	8.2
FC-C318	42.2	8.5	43.1	9.5	12.8	8.1	9.1	9.6
FC-218	41.0	9.1	45.0	15.0	11.7	6.6	9.0	9.5
HFC-32/125	39.0	9.2	45.3	10.0	12.1	7.2	9.2	8.6
NaHCO3	42.5	7.5	46.0	17.4	11.5	10.5	9.5	7.5
Alloy Avg.	38.6	9.1	42.8	13.9	11.6	7.3	9.1	8.2
Std. Dev.	3.0	1.2	2.6	5.5	1.6	0.9	0.6	0.7

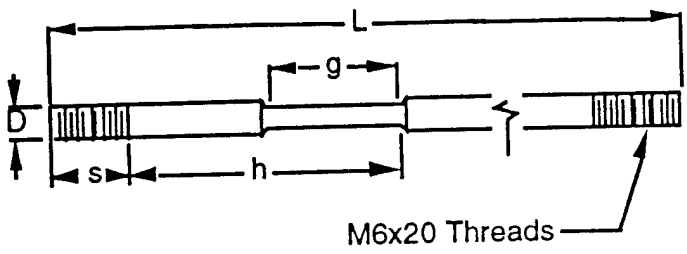
Table 4
Average Reduction in Area (%) in Each Agent at 150 °C as Compared to Ar at 150°C and Air at 25°C.

Environment	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130
Lab Air	78.1	50.9	73.7	76.7	66.3	69.4	48.6	52.1
Hot Ar	79.2	42.3	69.5	67.8	27.5	60.0	48.6	50.8
HCFC-22	80.2	37.7	74.1	67.9	31.6	62.0	50.1	47.8
HCFC-124	79.8	35.8	65.7	71.7	36.6	56.2	48.3	48.7
FC-31-10	80.2	39.9	67.7	66.9	38.2	59.8	51.4	47.0
HFC-227	79.5	39.1	68.9	69.8	43.3	61.1	48.7	48.2
HFC-125	80.4	39.4	67.3	68.7	40.0	61.9	48.6	49.2
FC-116	79.3	45.4	72.1	67.0	36.4	63.9	49.3	49.2
HFC-134a	80.3	39.0	69.9	69.0	31.1	59.6	50.4	49.6
HFC-236	78.4	41.0	68.9	66.8	33.7	60.2	45.7	47.6
FC-C318	79.9	40.9	68.5	65.0	33.0	61.1	47.5	48.5
FC-218	86.2	42.2	69.3	70.8	31.4	59.5	47.2	47.5
HFC-32/125	82.2	41.9	70.9	65.9	42.1	62.6	46.2	47.1
NaHCO3	80.1	35.2	68.4	56.3	33.8	58.1	51.5	44.3
Alloy Avg.	80.4	39.9	69.3	67.7	35.3	60.6	47.9	51.4
Std. Dev.	2.3	2.3	3.2	5.3	3.2	6.4	2.2	5.10

Table 5
Slow Strain Rate Tensile Test Rankings for Each Alloy/Agent Combination at 150 °C

Environment	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130	Agent Avg.	Std. Dev.	Agent Rank
HCFC-22	4	3	4	1	3	2	3	2	2.75	1.04	10
HCFC-124	2	3	2	1	3	3	2	1	2.13	0.83	5
FC-31-10	3	2	2	1	4	1	3	1	2.13	1.13	5
HFC-227	2	3	1	1	5	1	3	1	2.13	1.46	5
HFC-125	1	2	1	1	4	1	4	1	1.88	1.36	3
FC-116	1	2	2	1	3	1	2	1	1.63	0.74	1
HFC-134a	2	2	3	1	2	2	3	2	2.13	0.64	5
HFC-236	2	2	1	1	'	1	3	1	1.63	0.74	1
FC-C318	1	4	1	5	2	3	2	6	3.00	1.85	12
FC-218	3	1	2	1	2	1	3	3	2.00	0.93	4
HFC-32/125	2	2	2	1	5	2	4	1	2.38	1.41	9
NaHCO3	1	4	2	3	2	6	2	2	2.75	1.58	10
Alloy Avg.	2.00	2.50	1.92	1.50	3.08	2.00	2.83	1.83			
Std. Dev.	0.95	0.90	0.90	1.24	1.16	1.48	0.72	1.47			
Alloy Rank	4	6	3	1	8	4	7	2			

Rating	Freq	Interpretation
1	32	No evidence of environment influence.
2	32	Slight indication of possible environmental influence.
3	19	Some evidence.
4	8	Strong evidence.
5	3	Nature of interaction should be evaluated.
6	2	Nature of interaction should be evaluated.
7	0	Nature of interaction should be evaluated.
8	0	Nature of interaction should be evaluated.
9	0	Nature of interaction should be evaluated.
10	0	Nature of interaction should be evaluated.



D = 19 mm
L = 178 mm
g = 25.4 mm
h = 57 mm
s = 19 mm

Figure 1

Slow strain rate tensile sample design [6]

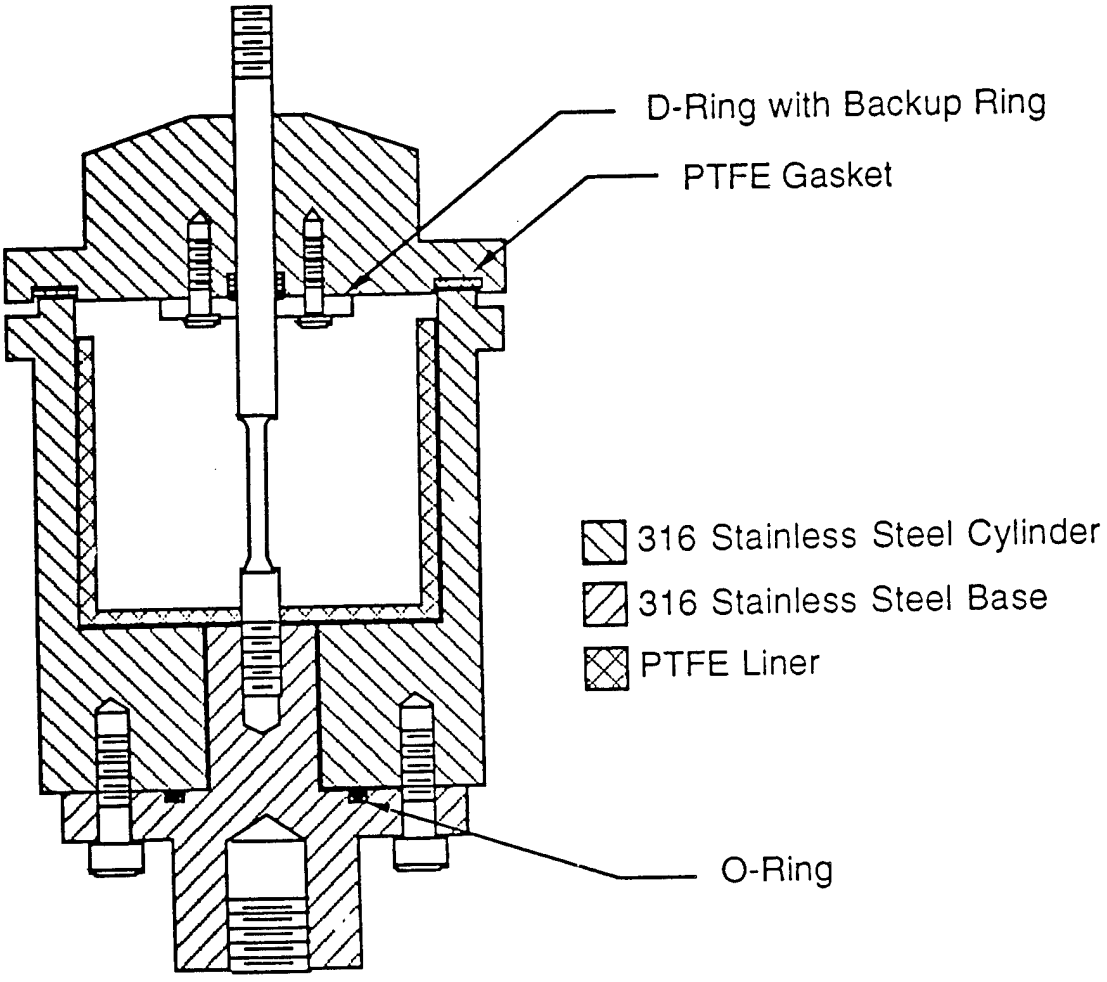


Figure 2

Slow strain rate tensile test chamber